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THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

V. THE HYDROGEN ENGINE AND THE NUCLEAR THEORY OF IGNITION[1]

By R. O. King,[2] W. A. Wallace,[3] B. Mahapatra[4]

Abstract

It should not be possible, according to the nuclear theory of ignition, stated in Part IV, to obtain ignition in the body of a gaseous combustible mixture by any method of heating if it remain truly homogeneous while the temperature is raised. Such mixtures cease to be homogeneous when heated by sudden compression to the temperatures required for ignition because of the formation of finely divided carbon by pyrolysis of lubricating oil or of hydrocarbon vapor. The finely divided carbon provides nuclear centers of ignition in the gaseous mixture. Ignition due to finely divided carbon produced by pyrolysis of the lubricant is demonstrated by experiments with hydrogen as the fuel for a C.F.R. engine. The usual pre-ignition and severe knocking were obtained when the engine in normal condition was run on hydrogen, and it was impossible, as previously found by others, to use any but weak mixtures even at low compression ratios. When however the combustion space was decarbonized and thereafter maintained reasonably clear of fluffy carbon, hydrogen could be used as the sole fuel at any compression ratio up to the limit of 10 : 1 possible with the engine, and at any mixture strength ranging from very weak to very rich, while power output varied accordingly. Conversely pre-ignition and combustion knock reappeared when carbon dust was admitted with the combustible mixture.

Introduction

Hydrogen–air mixtures when used in an Otto cycle engine are heated by sudden compression and by contact with hot surfaces such as exhaust valves. The tendency of the mixture to 'detonate' or to explode prematurely in the usual conditions of operation limits the power and efficiency to relatively low values. Ricardo (12), using the E35 engine, cylinder diameter 4.5 in., found that if the mixture with air contained 50% only of the hydrogen required for combining proportions, a compression ratio of 7 : 1 could be used and the high thermal efficiency of 37.5% obtained. It was necessary to lower the compression ratio progressively as the hydrogen concentration was increased but even so it was not possible to use the mixture strength for maximum power. "If an attempt were made to run with a rich hydrogen–air mixture, violent pre-ignition occurred, accompanied by firing back in the carburetor, which rendered further running impossible. Even with the compression ratio lowered to 3.8 : 1 the same thing occurred". There seemed to be a limiting indicated mean effective pressure (I.M.E.P.) of 74 lb. per sq. in. Attempts to obtain higher values by increasing hydrogen concentration or by raising

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the compression ratio were always defeated by the onset of detonation or pre ignition. The range of mixture strength usable with various engine fuels wa: discussed by Ricardo in a later publication (13, pp. 42–43) and, in respect o hydrogen, it was stated that "the range of burning could not be explorec because, so soon as any excess of hydrogen was admitted, back firing occurrec through the inlet valves". Ricardo's conclusions were confirmed by A. F Burstall (1) even in respect of the I.M.E.P. having a limiting value of approxi mately 74 lb. per sq. in. The experiments of Egerton, Smith and Ubbelohdc (4) with hydrogen as fuel for a Delco knock testing engine, cylinder diameter 2.5 in. only, demonstrated that knocking combustion was not restricted tc engines having relatively large cylinders. Egerton (4, p. 517) attributec the detonation to nitrogen peroxide formed from the nitrogen of the air.

The combustion phenomena described by Ricardo and others are usually attributed to ignition of the hydrogen–air mixture by hot surfaces or to ignition being the final result of a chain reaction proceeding at the temperature attained by sudden compression. An alternative explanation is afforded by the nuclear theory of self ignition advanced in Part IV (10), the finely divided carbon for nuclear centers of ignition, as required by the theory, being provided by pyrolysis of the lubricating oil. Experiments made accordingly in the Heat Engine Laboratory of the University of Toronto and described in Section I show that hydrogen can be used as the fuel for an Otto cycle engine, in any mixture proportion with air and at compression ratios rising to 10 : 1 without pre-ignition or detonation if the concentration of finely divided carbon in the gaseous mixture be maintained at a relatively low value.

Section I

Experimental

The Co-operative Fuel Research Committee (C.F.R.) knock testing engine was used for the experiments with hydrogen. The bore is 3.25 in. and the stroke 4.5 in. The compression ratio can be varied from 4 to 10 : 1. The cylinder is maintained normally at a nearly constant temperature of 212° F. by the evaporation of distilled water at atmospheric pressure. The engine is connected to a d-c. main generator and to a similar auxiliary generator. Speed is controlled manually by adjusting the field excitation of the main generator and the electrical output absorbed by a resistor bank.

Lubrication.—The piston is fitted with three pressure rings and one oil scraper ring. A partial vacuum is created in the crank case by fitting the breather with a nonreturn flap valve that closes during the compression and exhaust strokes. The rate of oil consumption in the circumstances is so low that, after 100 hr. running, careful measurement is required to determine the quantity used. The oil in the crank case was maintained at a temperature of between 120° and 130° F. by a manually controlled electric heater. A commercial brand of S.A.E. 30, without 'additives', was used during the experiments.

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Hydrogen Supply.—The standard horizontal carburetor with 9/16 in. diameter venturi and no throttle plate was used for the experiments. Hydrogen was admitted to the throat of the venturi through a 0.125 in. diameter hole in a screw which replaced the standard hold down screw of the unused cap jet. Hydrogen procured by electrolysis was supplied in the usual pressure bottles by the Dominion Oxygen Company, and contained not more than 0.3% of oxygen. The hydrogen passed through an adjustable pressure reducing valve, then through a fine adjustment needle valve to a circular square edged metering orifice in a thin plate and thence to the carburetor venturi. The rate of supply to the engine was taken to be proportional to the square root of the pressure difference, in inches of water, across the orifice.

Air Supply.—Air was taken in by the engine at laboratory temperature and the humidity not controlled. The standard air inlet to the carburetor comprises a short piece of 1¼ in. I.D. tubing ending in a 90° elbow into which is fitted a long inlet pipe (20½ in.) also 1¼ in. diam. Eight inches of the outer end is arranged as a silencer but the diameter of the tube is not reduced. The standard pipe inlet was on occasion replaced by a swirl chamber 6 in. diam. and 6½ in. long provided with tangential inlets and outlets. The cover of one end was a 'push on' fit and blew off when back firing through the carburetor (induction ignition) occurred.

The Inlet Valve.—The standard inlet valve is fitted with a 180° shroud so arranged that the combustible mixture is given a swirling motion on entering the cylinder. The arrangement has been found of beneficial effect in respect of determinations of the relative antiknock values of gasolines, but it reduces volumetric efficiency and is not used in practice.

Definition of the Terms Used to Describe Abnormal Ignition or Combustion

Detonation knock describes an effect due to the self-ignition and explosion of the gas ahead of the flame (end gas). Eliminating the knock by retarding ignition gives rise to a *decrease* of power.

Combustion knock describes an effect due to an abnormally high rate of flame propagation. The knocking sound in the C.F.R. engine is similar to that heard when detonation occurs. Eliminating or reducing the knock by retarding ignition gives rise to an *increase* of power. This characteristic makes it possible to distinguish between combustion knock and detonation knock.

Induction ignition describes the effect obtained when the combustible mixture ignites before the inlet valve closes. The effect gives rise to explosions in the induction system and carburetor, the violence depending on mixture proportion and the volume involved. The explosions occur irregularly.

Pre-ignition is initiation of combustion after the inlet valve closes and before ignition by spark. If the ignition occurs sufficiently late in the compression stroke, the engine will run without spark ignition but generally at reduced power and for relatively short periods of time.

Preliminary Engine Experiments with Unclean Combustion Chamber

The experiments were begun with the engine as found. It had been run for some weeks on hydrocarbon fuels, generally leaded. The compression ratio was set at 5 : 1, the ignition timing at 30° advance, and the engine run at 900 r.p.m. for a warming up period of one hour on leaded gasoline. The gasoline was then shut off* and hydrogen admitted at a sufficient rate to maintain the engine speed of 900 r.p.m., with light load. On increasing the rate of hydrogen supply and the load, severe knocking occurred, accompanied by occasional induction ignition. Thus the characteristics of hydrogen combustion in an engine as observed by Ricardo, Burstall, and Egerton had been recovered.

Very rich mixtures were then admitted. Combustion was silent and without induction ignition, just as when very weak mixtures were used. This interesting characteristic seems to have been overlooked by earlier experimenters.

It was observed during the experiments mentioned that knock always decreased on retarding ignition, while power increased; this indicated combustion knock rather than detonation knock.

The engine was dismantled for observation of the condition of the combustion chamber surfaces. The piston crown was found to be thickly coated with hard carbon. The piston ring grooves contained granular carbon but the rings were free. The exhaust valve was coated with a greyish white deposit. The inlet valve was fairly clean. The surfaces were thoroughly cleaned and the shrouded inlet valve replaced by a spare exhaust valve of the common tulip shaped type.

First Set of Trials with the Engine Combustion Space Initially Clean. Jacket Temperature, 212° F.; Compression Ratios Rising to 10 : 1, and Arbitrarily Chosen Ignition Timing

Preliminary trials were carried out after warming up the engine by running on leaded gasoline before changing over to hydrogen. There was then no induction ignition at any compression ratio within the range of the engine. Combustion was silent at compression ratios up to 8 : 1 but slight combustion knock occurred at 10 : 1 when using the mixture strength for maximum power. It developed later that ignition had been set too far advanced.

A complete set of trials was then carried out at compression ratios of 4.2, 6.0, 8.0, and 10 : 1 and with the hydrogen–air mixtures varying from very weak to very rich. It was supposed, judging from experiments made by others, that a considerable spark advance would be required for weak mixtures used at low compression ratios and less advance on increasing mixture strength and compression ratio, but nothing definite was known because previously it had not been possible to use anything but weak mixtures at any compression ratio. Trial spark settings of 30°, 20°, 10°, and 0° for the compression ratios mentioned were therefore used.

* *The engine was warmed up by running on gasoline in order to save hydrogen.*

The experimental results are given by the graphs of Fig. 1; net power output in kilowatts being plotted against rate of hydrogen supply. The values for rate of hydrogen supply are the square roots of pressure differences in inches

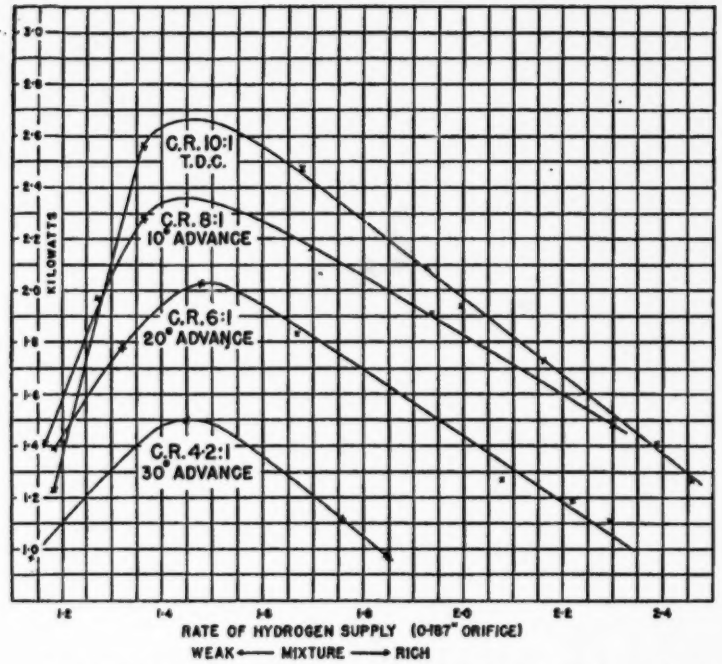

FIG. 1. *Relation between power output and mixture strength at compression ratios rising to 10 : 1. Jacket temperature, 212° F.*

of water across a circular square edged metering orifice, 0.187 in. diameter, in a thin plate. The graphs are of interest in showing for the first time on record that it is possible to run an engine on hydrogen in any proportion in a mixture with air at compression ratios rising to 10 : 1 and without any combustion difficulty as is evidenced by the consistent variations of power with changes of compression ratio and mixture strength.

Sundry Experiments and Recurrence of Induction Ignition and Knock

Air oscillation in the induction system of the C.F.R. engine is considerable and it appeared that some of the hydrogen supplied at the carburetor throat might accordingly be carried out of the standard inlet pipe to escape into the atmosphere. The standard pipe was therefore replaced by the swirl chamber.

The 0.187 in. diam. orifice for metering the hydrogen was replaced by one 0.125 in. diam. in order to obtain greater and more easily readable press differences, and for further convenience of reading pressure differences U-tube type of manometer was replaced by one of the single leg variety.

Experiments with hydrogen were resumed on completion of the chan mentioned, after the usual warming up of the engine by running for an h on leaded gasoline. The earlier combustion difficulties were again encounte and it was impossible to run with the 'correct' mixture strength, even at low compression ratio of 4 : 1, without violent explosions in the induct system. The difficulties were not overcome by replacing the swirl cham by the standard inlet pipe, by warming up the engine on unleaded gasoli or by approaching 'correct' mixture strength from the rich instead of weak side, or by lowering or raising the jacket temperature, or by tak precautions to avoid electric charges in the induction system possibly due the high velocity of the mixture passing over sharp edges.

The time of running since the first cleaning was about 12 hr. and the eng was dismantled for inspection of the combustion space and the valves. B valves were found to have been seating properly and were clean. T exhaust valve showed oxidation colors, brown and red. The piston ri were free but there was some loose carbon in the grooves. The water coo surfaces were free of loose carbon. The significant finding was a layer *fluffy carbon*, having the appearance of lamp black, on the piston crown. T combustion chamber, the inlet passageways, and the ring grooves w thoroughly cleaned and the engine reassembled for further trials.

Second Set of Trials, Combustion Space again Initially Clean. Jacket T perature, 212° F. Air Supply Through Swirl Chamber with Cover Off

The trials were made primarily to verify that the recurrence of combust difficulties was due to the fluffy carbon mentioned above. They were run compression ratios of 6, 8, and 10 : 1 and spark setting varied to determ optimum values in varying conditions of mixture strength and compress ratio. There was not a single case of induction ignition in the whole set trials; combustion was notably quiet except when using the mixture stren for maximum power at a compression ratio of 10 : 1. There was then sli combustion knock.

The experimental results are given by the three sets of graphs of Fig. It is of special interest that maximum power for any but the weakest richest mixture was obtained when ignition occurred at or very near top d center. At 10 : 1 compression ratio maximum power was obtained with spark 5° *retarded*. Regular ignition at this high compression ratio obtained by reducing the spark gap from the standard setting of 0.025 to 0.013 in. Maximum power at 8 : 1 compression ratio was obtained w a spark advance of 5°, whereas at the lower compression ratio of 6 : 1, optimum setting was at 0°, a somewhat inconsistent result justifying a rep tion of the experiments.

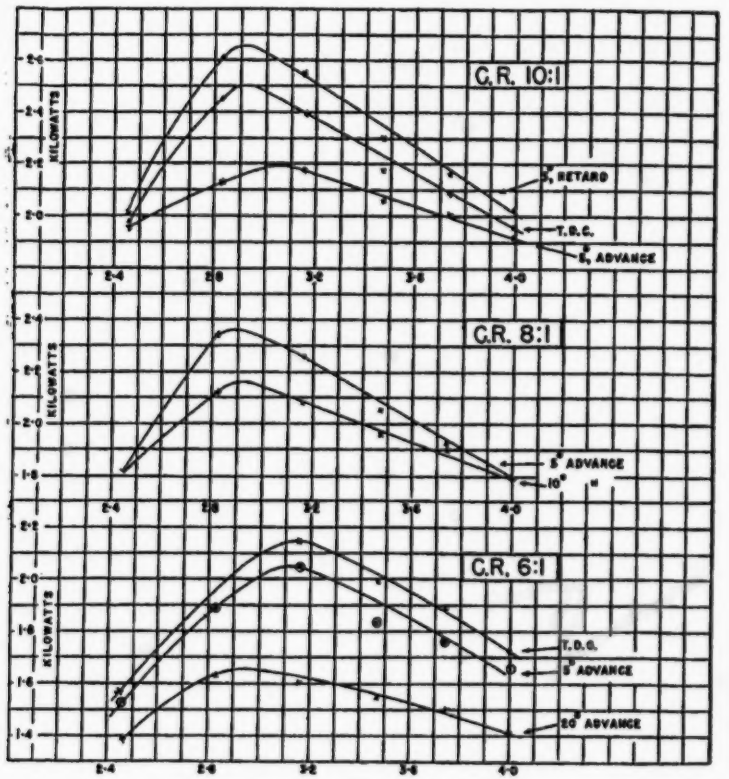

FIG. 2. *The effect of ignition timing on power output at compression ratios rising to 10 : 1. Jacket temperature, 212° F.*

Routine Cleaning Method

The experiments described above occupied about two hours' running time and no doubt the usual combustion difficulties would have recurred on continued running if no precaution had been taken to maintain the combustion space reasonably clear of fluffy carbon. A routine cleaning method was therefore adopted. Thus, always before starting a day's experiments the bouncing pin and spark plug were removed, the piston moved to top dead center, and the crown cleaned with a tooth brush inserted through the spark plug hole. The engine was then motored round to blow loose carbon through the holes mentioned. As a further precaution to avoid carbon formation by pyrolysis of hydrocarbon fuel the warming up period on gasoline was reduced to the time required to heat the jacket water to the boiling point and any further warming up done with hydrogen.

The engine was used after the adoption of the cleaning routine for a complete set of trials at low jacket temperature, extended trials using town gas and some sundry experiments made in preparation for future experimental work. There was no recurrence of combustion difficulties.

Third Set of Trials, Routine Cleaning of Combustion Space. Jacket Temperature, 95° to 100° F.

The experiments so far described were made with the standard C.F.R. method of evaporative cooling of the water jackets, that is, jacket water temperature was always 212° F. It is not customary to use such high temperatures in practice and as a matter of interest a set of trials was made with the jackets cooled by tap water, the flow being regulated to maintain an outlet temperature of 95° to 100° F. The standard C.F.R. air inlet pipe was used because it was found during the sundry trials mentioned above that slightly more power was obtained than when using the swirl chamber inlet, no doubt because of the ramming effect of the pipe.

The optimum spark setting for compression ratios of 4, 6, 8, and 10 : 1 was determined for varying mixture strengths. It was found that the optimum setting for the maximum power mixture strength was also the optimum for any richer mixture. But for mixtures on the weak side there would be some advantage in advancing the ignition progressively in accordance with the diminution of hydrogen concentration in the mixture with air.

The trials were made when using the optimum spark setting for the maximum power mixture strength. The experimental results are given by the graphs of Fig. 3. The running of the engine was exceptionally smooth and quiet even when using the mixture strength for maximum power at a compression ratio of 10 : 1.

It will be noted that the graphs are nearly parallel on the rich mixture side but not on the weak side, as would be expected from the finding that the optimum spark advance for the maximum power mixture was also the optimum for richer but not for weaker mixtures.

The Effect of Carbon Nuclei Added to the Hydrogen–Air Mixture

It has been demonstrated by the experiments so far described that induction ignition and combustion knock in the hydrogen engine are due to the igniting action of carbon nuclei derived from the pyrolysis of the lubricating oil. It became of interest, therefore, to observe the effect of carbon nuclei added to the entering gaseous mixture.

The carbon used for the experiments was pulverized charcoal screened with a 200 mesh sieve. It was described as having been activated by heating but had been standing open to the laboratory atmosphere for some weeks before

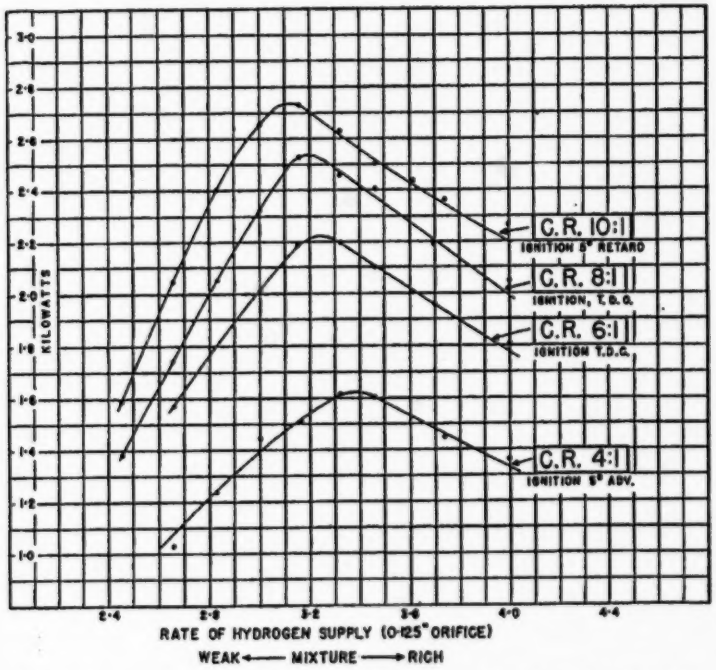

FIG. 3. *Relation between power output and mixture strength at compression ratios rising to 10 : 1, nearly optimum ignition timing. Jacket temperature, 95 to 100° F.*

being used for the experiments. The carbon was admitted to the air stream in advance of the carburetor throat, at a measured rate, by a device similar to a screw feed coal stoker. The experiment was begun with the combustion space in the condition maintained by the routine cleaning method. The standard pipe inlet was fitted and the jacket water maintained at 212° F. by the standard method.

The engine was started on hydrogen and run at a compression ratio of 6 : 1, with the mixture strength for maximum power and ignition at top dead center. There was no induction ignition, and combustion was silent. The carbon was then admitted at a rate of approximately 2.0 mgm. per stroke. Combustion knock occurred almost immediately and was followed by induction ignition accompanied by explosions in the induction system.

Preparations had been made to carry out a series of experiments to measure the rate of carbon supply required to induce premature ignition and combustion knock or detonation at compression ratios rising to 10 : 1, but, perhaps

as should have been expected, the carbon dust accumulated in the engine such an extent that induction ignition and combustion knock continued w the supply of carbon to the induction system was shut off.

Indicated Mean Effective Pressure and Indicated Thermal Efficiency

The experiments with the hydrogen engine are regarded as confirming nuclear theory of ignition. It is of importance, nevertheless, to show t confirmation was obtained while values of the indicated mean effect pressure (I.M.E.P.) and indicated thermal efficiency were such as would expected from the compression ratios and mixture strengths used during experiments.

The indicated power was determined by the motoring method. That the power required to motor the engine at the experimental speed of r.p.m. was measured immediately after cutting off the fuel supply and ad to the net power output measured previously. The method has been wid used by Ricardo and others, and, although it involves the unwarran assumption that engine friction is of the fluid variety and therefore independ of load, values obtained accordingly are useful for purposes of comparison

I.M.E.P.—The power required to motor the engine at 900 r.p.m., jac temperature 212° F., was determined after warming up, using benzene the fuel, at compression ratios of 6, 8, and 10 : 1. The piston area is 8.28 in., stroke 0.375 ft., and at 900 r.p.m.—

$$\text{I.M.E.P. (lb. per sq. in.)} = \text{Indicated horse power} \times 23.6.$$

Maximum power output being taken from the graphs of Fig. 2, the data gi in Table I are obtained.

TABLE I

INDICATED MEAN EFFECTIVE PRESSURES AT COMPRESSION RATIOS OF 6, 8, AND 10 : 1, WHEN USING THE MAXIMUM POWER MIXTURE STRENGTH

Compression ratio	Net output, kw.	Motoring power, kw.	I.H.P.	I.M.E.P., lb./sq. in.
10 : 1	2.66	1.61	5.73	136
8 : 1	2.36	1.59	5.30	125
6 : 1	2.15	1.48	4.87	103

Indicated Thermal Efficiency.—Relative rates of hydrogen supply reasonably accurate but approximate values only of quantities were obtain the metering orifice not having been calibrated. Thermal efficiencies c culated accordingly, again using data from Fig. 2, are given in Table II.

TABLE II

INDICATED THERMAL EFFICIENCIES; COMPRESSION RATIO, 10 : 1

Mixture strength	Net power, kw.	Indicated power, kw.	I.H.P.	Indicated thermal efficiency, %
15% rich	2.40	4.01	5.38	34.2
3% rich	2.64	4.25	5.70	39.8
Max. power	2.66	4.27	5.78	41.2
5% weak	2.58	4.19	5.62	42.4
17% weak	2.02	3.63	4.87	42.0

It will be noted from Table II that maximum efficiency was obtained for the mixture strength giving somewhat less than maximum power, as would be expected.

Section II

Discussion of Experimental Results

Induction ignition, normally described as "firing back through the carburetor", was obtained when, starting with a clean engine, sufficient time elapsed for an accumulation of fluffy carbon in the combustion space. The effect was not obtained if accumulation of the carbon were prevented. It is concluded that ignition of the fresh charge when obtained was due to glowing particles of carbon present in the residual charge.

Ignition by sudden compression.—The absence of the effect when the engine combustion space was nearly free of fluffy carbon is of interest in respect of experiments by others on the ignition of electrolytic gas ($2H_2 + O_2$) and hydrogen–air mixtures by sudden compression. Falk (5,6) concluded that the presence of lubricant (lanoline) was without effect on ignition temperature, but the experiments of Dixon, Bradshaw, and Campbell (2) and Dixon and Crofts (3) demonstrated that consistent ignition temperatures could be obtained solely when the lubricant was present as an extremely thin film on the surface of the combustion space, a condition set by the vacuum method of filling the space with the combustible mixture. Tizard (14), using the Ricardo compression ignition machine, similar to an engine cylinder, could not avoid the presence of a thin film of lubricant on surfaces exposed to the temperatures of compression and obtained ignition temperatures accordingly. When the Ricardo machine was redesigned to permit compression of the combustible mixture in a cylinder supposed to be free of lubricant, Tizard and Pye (15) were unable to obtain consistent ignition temperatures. Fenning (8), on continuing experiments with the machine, found that lubricant did in fact penetrate into the compression cylinder in an irregular manner. Thus, out of five compressions with a compression ratio of 9.2 : 1 and a jacket temperature of 97° C., two compressions resulted in premature ignition, two caused ignition after delay periods of 0.009 and 0.015 sec. and a fifth failed to cause ignition.

Nevertheless, when using the hydrogen engine at 10 : 1 compression ratio, a jacket temperature of 100° C. and more nearly adiabatic compression, the mixture failed to ignite prior to passage of the spark, if the combustion space were nearly free of finely divided carbon. That is, ignition did not occur in the body of the gaseous mixture in the absence of material nuclei of ignition as would be expected from the experiments of King (9) and King and Mole (11).

Flame velocity.—It is generally agreed that maximum engine power is obtained when maximum combustion pressure occurs about 12° after top dead center. It will be seen from Figs. 2 and 3 that at 10 : 1 compression ratio maximum power was obtained when the spark passed at 5° after top dead center. Combustion was thus completed in about 7° of crank angle, that is in 0.0013 sec., engine speed being 900 r.p.m. The flame would have traveled a distance equal to the diameter of the cylinder, 3.25 in., so velocity must have been approximately 63 m. per sec. even with no allowance for the time interval between passing the spark and the start of pressure rise. Flame velocity in the nearly clean combustion space of the engine is comparable with that observed by Fenning (7) when similar mixtures in a clean bomb were ignited by a spark, if allowance be made for differences in dimensions, initial temperature, and pressure. The flame velocity attained in the engine or bomb did not approach that of true detonation and in neither case was there any evidence of that phenomenon.

The pro-knock effect of carbon nuclei.—When hydrocarbon fuels, especially paraffins, are used in an engine, finely divided carbon can be derived from pyrolysis of the fuel, and maximum concentration occurs necessarily in the end gas [Part IV (10)]. Self-ignition can occur accordingly and nearly simultaneously throughout the mass of the gas; this results in detonation knock.

When hydrogen is used as the fuel, finely divided carbon can be obtained from the lubricating oil only and must be distributed by turbulence, more or less uniformly. There can be no preferential concentration in the end gas, consequently the sole effect of the carbon, after the passage of the spark, is to increase flame velocity and thereby promote combustion knock, an effect similar to that obtained by Fenning (7) on igniting electrolytic gas when the time from the passage of the spark to the attainment of maximum pressure was as short as 0.00072 sec., that is, combustion knock was obtained in the bomb on increasing flame speed by using electrolytic gas and in the engine by impregnating hydrogen–air mixtures with finely divided carbon.

Acknowledgments

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